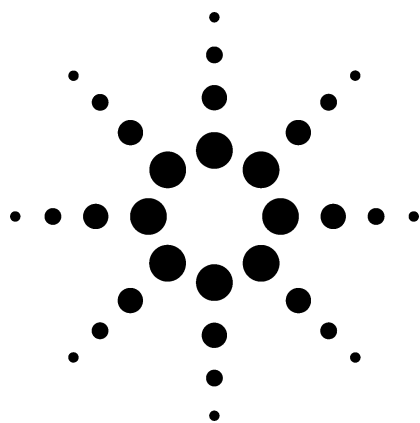


Empirical Formula Determinations and Compound-Independent Calibration Using a GC-AED System



Application

Atomic Emission Detector

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Abstract

A mixture of compounds containing carbon, hydrogen, and one or more heteroatoms was analyzed over several concentration ranges using an Agilent G2350A gas chromatograph-atomic emission detector (GC-AED) system. To verify the compound-independent response of the system, the percent relative standard deviation (%RSD) of the response factors for the individual elements was calculated. The results showed linearity of the entire system for a given element derived from a specific analyte, with the exception of runs with 0.1- μ L injections.

A mixture of 16 organochlorine pesticides was analyzed at the 40-ng/ μ L level. Empirical formulas were calculated for each analyte. Generally, the calculated formulas were found to agree with the actual formulas.

Introduction

Results of the first Agilent gas chromatograph-atomic emission detector (GC-AED) system were published in 1990.^{1,2} A second-generation system,³ the G2350A, which utilizes a moving grating and fixed diode array, is described in this application note. The system consists of an Agilent 6890 Series GC, an Agilent AED, and an Agilent AED ChemStation.

The GC-AED produces element-specific chromatograms based on light emission. The sensitivities of the elements differ from each other in emission intensity. In general, the sensitivity for any element compares favorably with that produced by other GC detectors.

The selectivity of a given element is dependent on interferences from carbon, usually in the form of CO molecular emissions. In many cases, selectivities from GC-AED are better than those of other GC detectors. GC-AED is now widely used in analytical laboratories.

A major benefit of using the GC-AED is its nearly compound-independent response.⁴⁻⁷ Compound-independent calibration (CIC) can save laboratories significant time and cost. Many of the required standards are costly, and multicomponent mixtures are time-consuming to prepare. Other standards are hazardous or extremely difficult to obtain. Another benefit of the GC-AED is that the system can estimate the quantity of an unknown element present in a sample.

A direct result of compound-independent response is the ability to measure elemental mole ratios (EMR). If these ratios were perfect, they would result in empirical formulas. For unknowns, the response on each AED channel can be compared to the response of one or more standards. The ratio of these responses to a standard is used to determine EMR. The accuracy of these EMR has been established.⁵⁻⁸

The experiments described in this application note were performed to determine the CIC and EMR capability of a second-generation GC-AED.



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Experimental

The GC and AED operating conditions are shown in table 1. Helium carrier gas was used for all analyses. All injections were performed using a 5- μ L syringe and a G1916A autosampler. The injection port was fitted with a single taper liner containing a small amount of glass wool (part number 5062-3587).

Data reduction was accomplished using the standard data analysis software supplied with the system, G2360AA, rev. A.01.02. This software includes extensive CIC options. CIC can be done using multiple peaks from multiple runs. EMR calculations can be referenced to any element.

To demonstrate typical performance, the GC-AED system was not optimized prior to or during this study. The liner had been used for about 3 weeks and exposed to a wide variety of sample types, and the discharge tube had been in use for 2 weeks. Prior use of the columns was unknown.

Table 1 lists the wavelengths used for CIC. The AED checkout sample (AEDCS) was used to calibrate the instrument for CIC. Figure 1 shows the multielement chromatogram of the AEDCS.

For EMR data acquisition, the elements in Set A only were used for the analysis.

One microliter of the AEDCS was injected at each split ratio listed in table 1 for CIC. Additionally, 0.5- and 0.1- μ L injections were made at 173:1.

Table 1. Instrument Operating Conditions

G2350A Atomic Operating Conditions			
Set A		Set B	
Element	Wavelength nm	Element	Wavelength nm
Carbon	496	Deuterium	656
Hydrogen	486	Nitrogen	174
Chlorine	479	Silicon	252
Oxygen	171	Fluorine	690
Sulfur	181	Bromine	478
CIC		EMR	
Cavity temperature (°C)	250	400	
Transfer line temperature (°C)	250	300	
Solvent vent on (min)	0.02	0.02	
Solvent vent off (min)	1.4	1.4	
Reagent gas pressures (psi) (EPC)			
Hydrogen	18	18	
Oxygen	33	33	
Auxiliary	25	25	
6890 Series Gas Chromatograph			
	CIC	EMR	
Injection volume (μL)	0.1, 0.5, 1.0	1.0	
Split ratio (x:1)	8.65, 17.3, 34.6, 86.5, 173	50	
Column	HP-INNOWax	HP-35	
Part number	19091N-133	19091G-133	
Dimensions	30 m × 0.25 mm × 0.25 μm	30 m × 0.25 mm × 0.25 μm	
Initial temperature (°C)	60	160	
Initial time (min)	0	1.0	
Ramp (°C/min)	30	10	
Final temperature (°C)	180	280	
Final time (min)	1.0	0	
Run time (min)	5	13	
Column flow (mL/min)	2.0	2.0	
Column head pressure (psi)	21.5	28.8	
Inlet temperature (°C)	250	280	

The 0.1- μ L injections showed good precision but poor accuracy. Four additional 0.1- μ L injections of the AEDCS were made at 173:1 and at 34.6:1. Also, for comparison, four 1.0- μ L injections were made at these two split ratios.

One analysis of the pesticide mixture was done for EMR using the conditions listed in table 1.

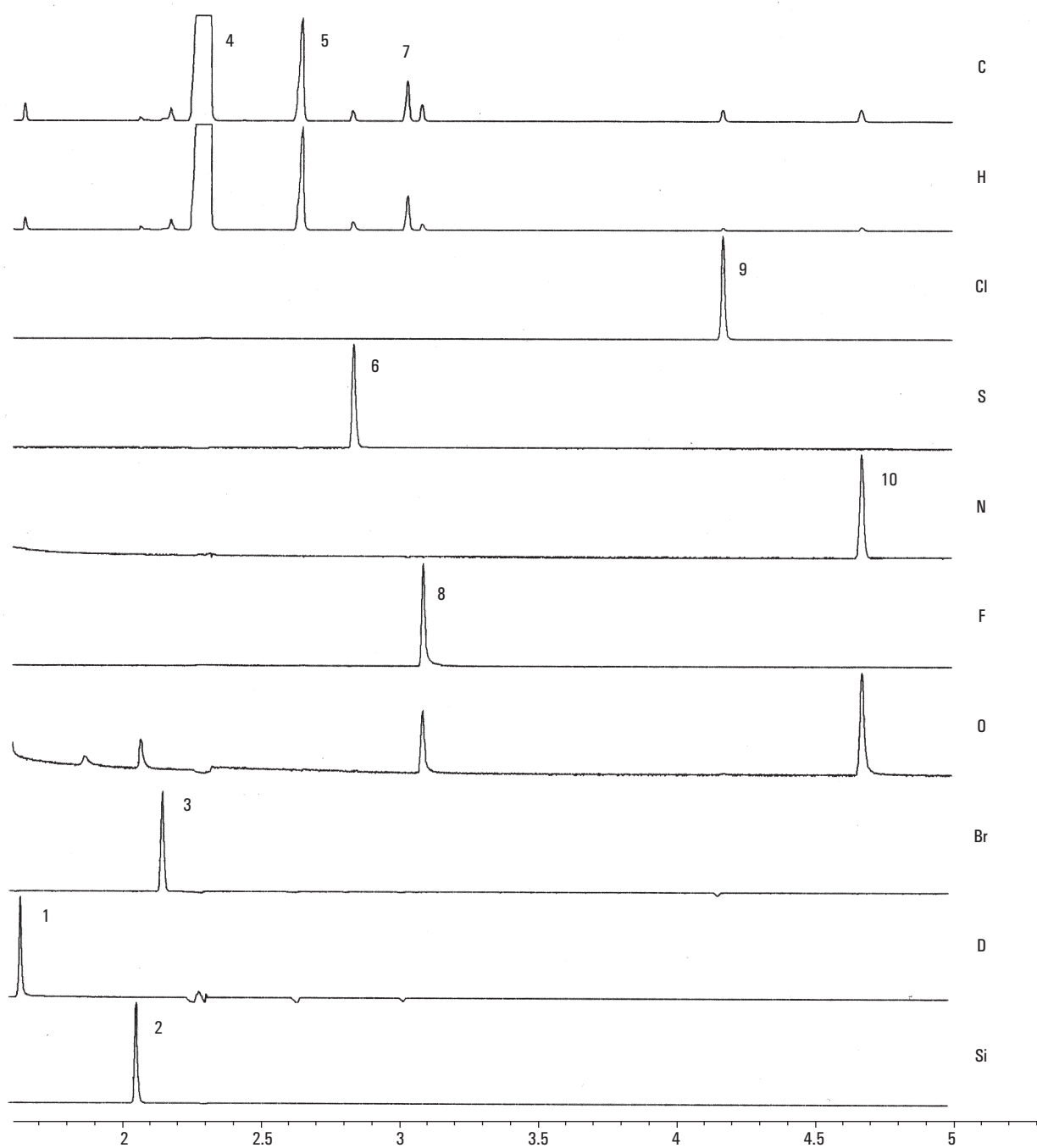


Figure 1. GC-AED Multielement chromatogram of the AED checkout sample on HP-INNOWax (peak identifications are listed in table 2.)

CIC Results

Response factors (RFs) were calculated using the following formula:

$$RF = \frac{(\text{ng}/\mu\text{L}) \times (\mu\text{L-injection}) \times 1000}{(\text{split ratio}) \times (\text{area})}$$

The percent relative standard deviation (%RSD) determined from the RF calculations on seven analyses are listed in table 2. This indicates the linearity of the entire system for a particular element derived from a specific analyte.

Careful examination of the chromatograms shows some integration errors. All integrations were done automatically without manual correction to illustrate typical laboratory use. However, integration errors could not account for the large deviations. It was noted that all RFs for the 0.1- μL injections were consistently low by about 30 percent, and the peak areas were too high. The cause of the low RF values is being investigated.

The data indicate, therefore, that the response factor reproducibility is better for 1.0- μL injections. Table 3 shows the results of the 16 additional analyses performed: four 0.1- μL injections and four 1.0- μL injections at two different split ratios.

Table 2. Percent RSD of Response Factors for Compound-Independent Calibration

Peak Fig 1	Compound	Carbon %RSD	Hydrogen %RSD	Oxygen %RSD	Heteroatom %RSD
1	n-Decane	5.7	Perdeuterated		17
2	Tetraethylorthosilicate	15	11	9.2	16
3	1-Bromohexane	13	13		4.9
4	n-Dodecane	9.1	6.0		
5	n-Tridecane	4.8	8.4		
6	t-Butyl disulfide	6.8	16		6.6
7	n-Tetradecane	5.4	7.0		
8	4-Fluoroanisole	6.9	7.1	7.7	26
9	1,2,4-Trichlorobenzene	6.2	8.8		4.2
10	Nitrobenzene	5.9	7.7	12	12

%RSD - Percent relative standard deviation of response factors for a single compound from

7 different injections, each at a different injection volume or split ratio

- Carbon ng on column range from tetraethylorthosilicate (0.1–20 ng) to n-dodecane (15–3000 ng)
- Hydrogen ng on column range from 1,2,4-trichlorobenzene (0.0056–1.11 ng) to n-dodecane (2.6–520 ng)
- Oxygen ng on column range from 4-fluoroanisole (0.033–6.6 ng) to nitrobenzene (0.072–14.4 ng)

Table 3. Precision Comparison of 0.1- μL versus 1.0- μL Injections

	Range of %RSD Carbon RF Dependent on Compounds		
Split Ratio 173:1			
0.1- μ L injections	0.4	to	14.6
1.0- μ L injections	0.9	to	3.0
Split Ratio 34.6:1			
0.1- μ L injections	0.7	to	6.0
1.0- μ L injections	1.7	to	2.8

Table 4 shows the RF %RSD at each injection volume and each split ratio for the original seven injections across all compounds. It also shows the RF %RSD for all compounds for all injections except the 0.1- μ L level. The last row of numbers in the table approximates the error in quantifying any of the injected analytes at any level from any other analyte at any level. These errors may seem large, however, the following should be considered:

1. There is no system optimization.
2. Structures include n-alkanes, substituted alkanes, and aromatics.
3. The concentration range for carbon is 0.1 to 3,000 ng and for hydrogen is 0.0056 to 520 ng, which both exceed the published dynamic range.
4. Many oxygen measurements are below the published detection limit, and only three compounds contain oxygen.

The last set of measurements on the AEDCS determined minimum detection limits (MDLs). These are normally calculated automatically from the system software using peak heights and noise. It was of interest to determine the amount that a minimum measurable area would represent. Injections of 0.5 or 1.0 μ L were made at various split ratios until the peaks merged into the baseline. The results are shown in table 5. Measured values are shown in pg, as is common practice.

The GC-AED system meets Agilent specifications when measured using the system software.

Table 4. RF Percent RSD Across All Compounds for Each Injection

Injection Volume μ L	Split Ratio	Carbon %RSD	Hydrogen %RSD	Oxygen %RSD
0.1	173	6.4	19	1
0.5	173	2.7	16	25
1.0	173	2.6	6.9	16
1.0	86.5	2.9	6.2	12
1.0	34.6	7.0	5.9	9.0
1.0	17.3	12	7.1	6.1
1.0	8.65	11	6.1	4.6
All Except 0.1- μ L Level		9.4	11.2	16

Table 5. Measured MDLs Based on Area Versus Published Specifications

Element	Measured (pg)	Published (pg/sec)
Carbon	47	1 ($\lambda = 193$)
Hydrogen	7	4
Oxygen	74	150
Nitrogen	6	30
Chlorine	34	30
Bromine	58	18 (not a spec)
Sulfur	0.7	2
Phosphorus	1	2

EMR Results

Elemental mole ratios (EMR) can be calculated using the standard Agilent AED ChemStation CIC software.

A mixture of 16 organochlorine pesticides was analyzed. The concentration of each analyte was 2,000 ng/ μ L. At a split ratio of 50:1, 40-ng samples of each pesticide were injected on column. The pesticide multielement chromatogram is shown in figure 2. The pesticide formulas and retention times are listed in table 6.

The system was calibrated using α -BHC. EMR were calculated for each pesticide based on this calibration. The calibration and calculation procedure were repeated for all 16 pesticides.

As it is not practical to show all 240 (16×15) results, a percent error was determined for each ratio of carbon:element. For example, the actual C:Cl ratio for γ -BHC is 1:1. Using α -BHC for calibration, the calculated C:Cl ratio for γ -BHC is 1:0.999—an error of 0.1 percent.

The averaged error percentages are shown in table 7. These include all ratios for all elements relative to carbon for the 16 analytes. The largest error was seen when calibrating on endosulfan sulfate. The area on the oxygen chromatogram was clearly too low (figure 2). Therefore, the averaged percent error for oxygen across all analytes excluding endosulfan sulfate is also shown.

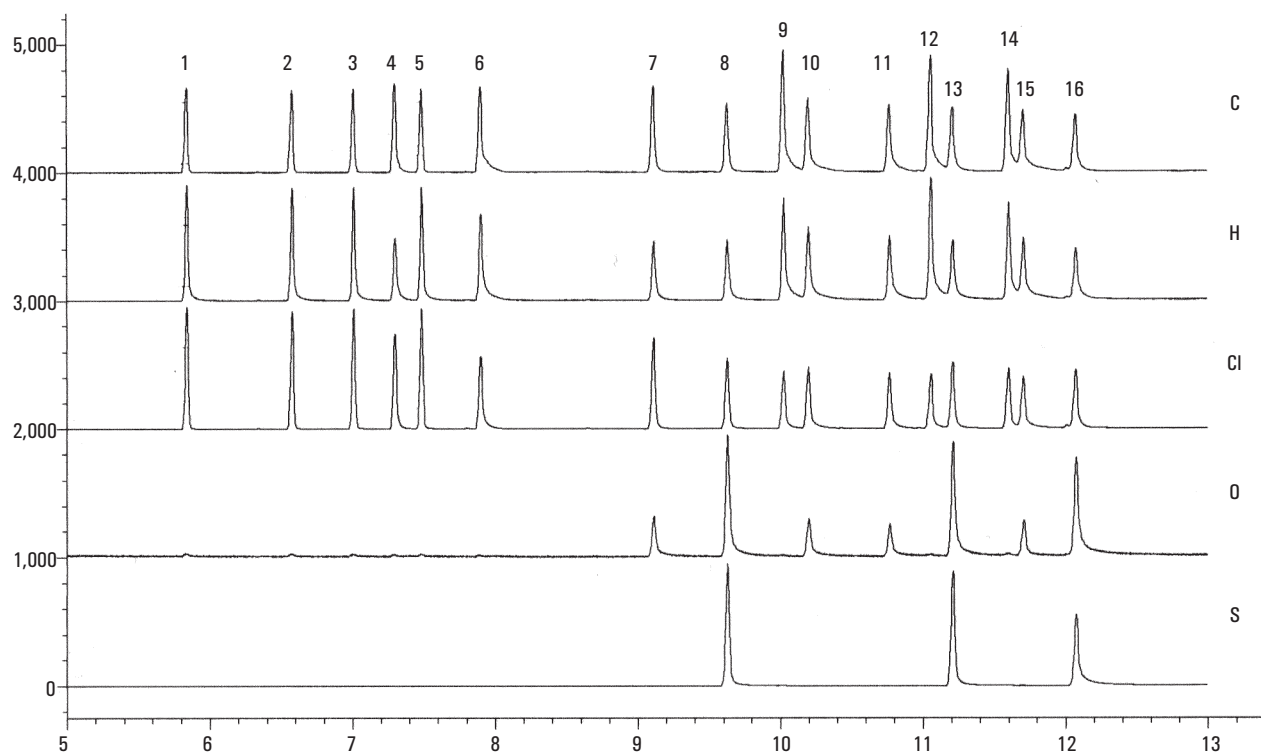


Figure 2. GC-AED Multielement chromatogram of 16 pesticides on HP-35. (Peak identifications are listed in table 6.)

Conclusions

The Agilent GC-AED system is suited to compound-independent calibration. Calibration for a given element can be performed, within limits, using one or more compounds at different levels. Response of analytes not specifically calibrated can be measured and quantified. The error on these measurements is element-dependent and generally ranges from 5 to 15 percent.

Response can be varied by changing split ratio or injection volume. However, 0.1-μL injection volumes should only be used if the volume is held constant. For best precision, the glass wool plug should be positioned near the top of the injection port liner. This allows the syringe needle to be wiped off.

The elemental mole ratio of an unknown can be measured after calibrating the system with one or more known compounds. EMR accuracy is dependent on the response of both the calibration compounds and the unknown. These responses should be kept as close as possible on each channel. For compounds of similar structure, the EMR errors are typically less than 10 percent.

Elemental mole ratios are very valuable for laboratories that use GC-mass spectrometry (GC-MS) to detect the presence of a particular element and its amount relative to other elements, or to detect the absence of a particular element. If a GC-MS laboratory requires GC-AED results displayed on a GC-MS system, a supplemental software program is available that converts AED data to a GC-MS readable format.

Table 6. Pesticides Analyzed for EMR

Peak	Pesticide	Formula	Retention Time (min)
1	α-BHC	C ₆ H ₆ Cl ₆	5.84
2	γ-BHC	C ₆ H ₆ Cl ₆	6.58
3	β-BHC	C ₆ H ₆ Cl ₆	7.01
4	Heptachlor	C ₁₀ H ₅ Cl ₇	7.30
5	δ-BHC	C ₆ H ₆ Cl ₆	7.49
6	Aldrin	C ₁₂ H ₈ Cl ₆	7.90
7	Heptachlor epoxide	C ₁₀ H ₅ Cl ₇ O	9.11
8	Endosulfan I	C ₉ H ₆ Cl ₆ O ₃ S	9.63
9	4,4'-DDE	C ₁₄ H ₈ Cl ₄	10.03
10	Dieldrin	C ₁₂ H ₈ Cl ₆ O	10.20
11	Endrin	C ₁₂ H ₈ Cl ₆ O	10.77
12	4,4'-DDD	C ₁₄ H ₁₀ Cl ₄	11.06
13	Endosulfan II	C ₉ H ₆ Cl ₆ O ₃ S	11.21
14	4,4'-DDT	C ₁₄ H ₉ Cl ₅	11.60
15	Endrin aldehyde	C ₁₂ H ₇ Cl ₆ O	11.71
16	Endosulfan sulfate	C ₉ H ₆ Cl ₆ O ₄ S	12.07

Table 7. Averaged Percent Error from Pesticide EMR, Normalized to Carbon

Element	Percent Error
Hydrogen	2.2
Chlorine	3.3
Oxygen	10
Oxygen	6.3*
Sulfur	5.8

* Excluding Endosulfan sulfate

The GC-AED system can be used by an analytical laboratory as a replacement for multiple GC systems with specific detectors.

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